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Initial-State Shift of the Carbon 2s Levels of Chemisorbed Hydrocarbons on Nickel

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(Received 14 November 1977)

uv photoemission results using filtered $h\nu = 40.8$-eV radiation show strong shifts in the low-lying $C(2s)$-derived levels of chemisorbed hydrocarbons on Ni relative to the higher-lying σ levels. These differential shifts provide evidence for initial-state potential and/or rehybridization effects which are important in interpreting high-lying valence orbital shifts and the bonding of chemisorbed species.

Here, I present filtered $h\nu = 40.8$-eV photoemission results for chemisorbed hydrocarbons on Ni which show a new type of chemisorption-induced shift in the low-lying $C(2s)$-derived states that has not been detected for other chemisorption systems. Namely, I find that the ionization levels of the low-lying $C(2s)$-derived σ states are shifted by ~ 1 eV to larger electron binding energies and broadened relative to the ionization levels of the σ_{CC}- and σ_{CH}-derived states—a similar effect as observed for the π orbitals.[1] These low-lying $C(2s)$-derived valence states for chemisorbed hydrocarbons have not been observed previously, nor have they been explicitly considered theoretically despite numerous recent calculations to understand better the bonding and energy level shifts of chemisorbed hydrocarbons.[2]

I present evidence that these differential σ-level shifts arise in the initial state and are the result of either the asymmetry of the potential at the surface or surface-induced molecular rehybridization. Such effects not only are important

in understanding the bonding of hydrocarbons to surfaces but may also be present in other systems. Thus, these results are of general importance for interpreting and relating high-lying valence orbital shifts of chemisorbed species to chemical bonding.[1,3,4]

The experimental system is the same as that described elsewhere,[5] while the procedures used to prepare and clean the Ni(111), (100), and (110) samples have also been described previously.[1,5] Note that the higher reactivity of the (100) and (110) surfaces requires the study of chemisorption on these surfaces at low temperatures ($T \sim 100$ K). Purified reagent-grade hydrocarbons or ultrahigh-purity gases were used and checked for impurities by mass spectroscopy. The photoemission measurements were performed with a new high-intensity dc resonance lamp equipped with a 200–300-Å carbon filter which completely suppressed the He I ($h\nu = 21.2$ eV) radiation so as to obtain essentially pure He II ($h\nu = 40.8$ eV) radiation as done in gas-phase studies.[6,7] Typical

count rates from the Ni d bands for the filtered
He II angle-integrated studies with a cylindrical
mirror analyzer were 50 000 counts per second
for 0.25-eV resolution. The light-source–sample–
analyzer geometry is also identical to that de-
scribed elsewhere.[5] Finally, I believe that my
results are characteristic of angle-integrated
spectra as I see insignificant energy shifts in the
adsorbate ionization levels for rotation and/or
tilting of the sample relative to the light beam
and energy analyzer which are both fixed.

I present results here for chemisorption on the
Ni(100) surface which are qualitatively similar to
my results for the (111) and (110) Ni surfaces.
In Fig. 1(a) I show a composite of the filtered
He II $N(E)$ spectra for a near-saturation exposure
of benzene ($\Delta\varphi = -1.2$ eV) to Ni(100) at $T \sim 100$ K.
In Fig. 1(b), I show the difference in emission
$\Delta N(E)$ after chemisorption as determined from
direct subtraction of the $N(E)$ spectra of the clean
and benzene-covered surface. For comparison
I also show the $\Delta N(E)$ and $N(E)$ spectra in Fig.
1(c) for a thick layer of condensed benzene (ob-
tained under identical conditions) and two gas-

FIG. 1. Photoemission spectrum $N(E)$ at $h\nu = 40.8$
eV for (a) clean Ni(100) ($\varphi = 5.2$ eV) and for chemi-
sorbed benzene on Ni(100) formed after a 4×10^{-6} Torr-
sec exposure of benzene to Ni(100) at $T \sim 100$ K ($\Delta\varphi$
$= -1.2$ eV). Comparison of the relative level positions
of the $\Delta N(E)$ spectrum for (b) chemisorbed benzene
are made with those of (c) condensed and gaseous ben-
zene (Refs. 7 and 8) where I have labeled the principal
orbital character of the ionization levels. (Here σ de-
notes equal σ_{CH} and σ_{CC} character.)

phase spectra. The first gaseous spectrum (sol-
id line) was obtained with a similar energy ana-
lyzer, energy resolution, and light-beam/ana-
lyzer geometry as used here.[8] The second spec-
trum (dashed line) was obtained under different
conditions in a higher resolution spectrometer.[7]

In order to facilitate comparison of the levels
of chemisorbed benzene to gaseous and condensed
benzene and to account roughly for initial-state
screening and final-state relaxation effects,[1,9] I
have shifted the latter spectra toward smaller
binding energies so as to align arbitrarily the
high-lying σ_{CC}- and σ_{CH}-derived levels. I also
indicate in Fig. 1 the principal orbital charac-
ter(s) of the benzene levels in the high-resolution
gas-phase spectra as determined from ground-
state calculations I have made using an ab $initio$
SCF (self-consistent-field) Hartree-Fock LCAO
(linear combination of atomic orbitals) method[10]
(Gaussian-70) with a 4-31G basis set. Here, the
molecular orbitals derived primarily from C(2s)
atomic orbitals are denoted as ss orbitals.

From the relative level positions in Fig. 1, I
observe that chemisorption has caused signifi-
cant orbital-dependent shifts in the low-lying ion-
ization levels of the free benzene molecule which
were not observed in previous studies.[1] Namely,
in addition to a 1.2-eV shift of the π level of
chemisorbed benzene, the ss levels are also
shifted by 0.7, 0.6, and 0.3 eV, respectively,
relative to the more uniformly shifted σ_{CC} and
σ_{CH} levels. Designating the xy plane as the mo-
lecular plane, I note that the levels derived from
either the C(2p_z) atomic orbitals (π levels) or the
C(2s) atomic orbitals (ss levels) are shifted rela-
tive to those derived from the C(2$p_{x,y}$) atomic or-
bitals (σ_{CC} and σ_{CH} levels). Molecular orbitals
having both C(2s) and C(2$p_{x,y}$) atomic components
appear to be shifted according to the degree of
admixture as seen for the four lowest lying val-
ence levels of benzene (Fig. 1) which have de-
creasing C(2s) character and increasing C(2$p_{x,y}$)
character with decreasing binding energy. I also
find additional level broadening (~ 0.3 eV) for the
lowest lying ss level.

I observe similar shifts in the valence levels of
other unsaturated hydrocarbons chemisorbed on
Ni, but not for the saturated hydrocarbons which
only physically adsorb on Ni at low temperatures.
Specifically, in Fig. 2, I show the ionization spec-
tra of gaseous and chemisorbed C_2 hydrocarbons
on Ni(100). Again, the ionization levels of the π
and C(2s)-derived levels are shifted to larger
binding energies relative to the σ_{CC}- and σ_{CH}-de-
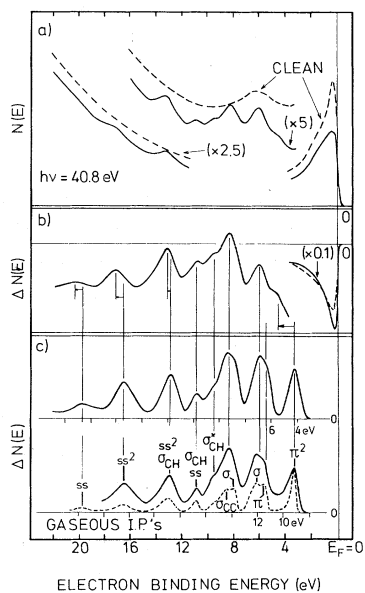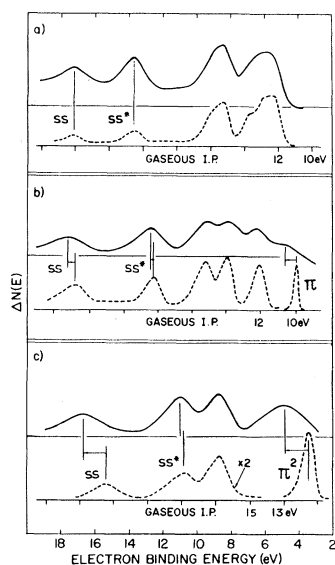
FIG. 2. Comparison of the photoemission difference spectra $\Delta N(E)$ for near-saturation coverages (4×10^{-6} Torr-sec exposure) at $T \sim 100$ K of (a) physisorbed ethane, (b) chemisorbed ethylene, and (c) chemisorbed acteylene to their respective gas-phase ionization spectra. The gas-phase spectra for ethylene and acetylene were obtained in a gas-phase spectrometer of similar geometry and resolution as mine (Ref. 8) while that for ethane was obtained in a higher resolution spectrometer (Ref. 6).

rived ionization features. Here, the ss^* levels of acetylene and ethylene have less $C(2s)$ character and more $C(2p_{x,y})$ character, and are less strongly shifted than the ss levels. The preferential level broadening of the ss levels of acetylene and ethylene (~ 0.7 and 0.3 eV, respectively) are more clearly observed here than for benzene.

A variety of initial- and final-state effects can occur together so as to shift molecular ionization levels upon adsorption.[1,9] However, the differential shifts observed here for the $C(2s)$-derived levels relative to the $C(2p_{x,y})$-derived levels are characteristic of rather specific initial-state effects which for these cases appear to be larger than, for example, orbital-dependent relaxation effects.

Neither orbital-dependent extramolecular relaxation effects for the $C(2s)$- versus the $C(2p)$-derived states nor chemisorption-induced geometry changes are consistent with the observed differential level shifts. Namely, greater extramolecular relaxation for the lower-lying, more corelike states—as observed for the $C(2s)$-derived orbitals of certain organic molecules on ZnO,[3] as well as predicted for the more corelike

orbitals of CO and Ni[11] and found for CO on Pt(111)[12]—is expected to shift the $C(2s)$-derived states in an opposite sense to that observed here. An opposite shift would also occur for orbital-dependent relaxation effects arising within either of two screening models: an image-charge screening model[13] where the molecule lies flat on the surface, or a molecularlike screening model.[14] Finally, comparisons of calculated molecular orbital eigenvalues for free and distorted molecules show that the large shifts in the lowest lying $C(s)$-derived levels are not consistent with any likely geometry of benzene or the geometry of ethylene as deduced from the higher-lying σ_{CC}- and σ_{CH}-derived levels. We note that vibrational loss spectroscopy for benzene chemisorbed on Ni(100) also suggests only small geometry changes upon chemisorption.[15]

The observed differential level shifts for these low-lying $C(2s)$-derived states are consistent with an orbital-dependent initial-state potential shift. The initial-state potential is known to shift the core levels of implanted rare-gas atoms by $2-3$ eV to larger binding energies.[16] At a surface the asymmetry of the potential, i.e., the surface barrier, can cause orbital-dependent valence level shifts of $1-2$ eV as theoretically found for the $3s$, $3p_z$, and $3p_{x,y}$ orbitals of Si.[17] For a molecule on a surface, we also expect similar differential shifts which would depend upon the orientation of the molecule and its orbitals on the surface. Under the assumption that the likely case that the hydrocarbon molecule lies parallel to the surface in the xy plane, the orbitals derived from $C(2p_z)$ and $C(2s)$ atomic components will be shifted to larger binding energies relative to those derived from $C(2p_{x,y})$ atomic components. The relative magnitudes as well as the orbital character dependence of the observed differential level shifts for the $C(2s)$-derived levels, e.g., the four ss levels of benzene, are well explained by this type of initial-state effect. We also expect a potential shift for the π levels comparable to or greater than that for the purest $C(2s)$-derived states. Finally, the observed broadening of the shifted $C(2s)$-derived levels may arise from more efficient Auger neutralization, i.e., shorter lifetimes, for these photoionized states than those derived from the higher-lying valence states.

The relative shift of the $C(2s)$-derived levels can also arise from the rehybridization of the $C(2s)$ and $C(2p_z)$ atomic orbitals during bonding —driven by the surface potential[18] and/or covalent bonding. Such an effect is found to occur in

411

the SCF Hartree-Fock LCAO calculations[10] (Gaussian-70) of acetylene and ethylene bonded in a variety of geometries on one- to four-atom Be clusters. Here, rehybridization in conjunction with charge rearrangement shifts the π and ss levels to larger binding energies relative to the σ levels. Such rehybridization would imply that the $C(2s)$ atomic orbitals play an important role in bonding. Clearly, more detailed theoretical calculations are necessary to understand fully the $C(2s)$ shifts observed here and discriminate between these two possible effects.

In summary, new results are presented which show unusual differential level shifts and broadening of the low-lying $C(2s)$-derived states of chemisorbed hydrocarbons on Ni. I provide evidence that these differential shifts arise in the ground state from an initial-state potential effect and/or a rehybridization effect associated with a new mode of bonding. Such effects may occur in other chemisorption systems and are important in interpreting valence orbital energy-level shifts and the nature of bonding from photoemission measurements. For example, the π-level shifts for chemisorbed hydrocarbons (or the 5σ level shift of CO) can occur independent of the bonding mechanism via potential shifts and/or rehybridization effects. Such nonchemically specific effects would explain why similar high-lying orbital "bonding" shifts are observed for adsorbates on different substrates, such as Cu or Ni, despite expected differences in the nature and/or strength of the chemisorption bonding interaction.[4]

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